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Ethanol oxidation on Pt single crystal electrodes: Surface structure effects in alkaline medium

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Ethanol oxidation in 0.1 M NaOH on single crystal electrodes has been studied using electrochemical and FTIR techniques. The results show that the activity order is the opposite of that found in acid solutions. The Pt(111) electrode displays the highest currents and also the highest onset potential of all the electrodes. The onset potential for the oxidation of ethanol is linked to the adsorption of OH on the electrode surface. On the other hand, very small (or even negligible) amounts of CO_{ads} and carbonate are detected by FTIR, which implies that the cleavage of the C-C bond is not favored in this medium. The activity of the electrodes diminishes very fast upon cycling. The diminution of the activity is proportional to the measured currents and is linked to the formation and polymerization of acetaldehyde, which adsorbs on the electrode surface and prevents further oxidation.

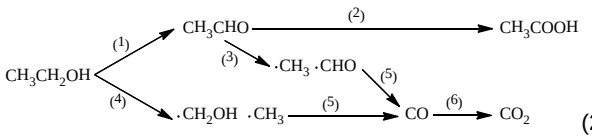
1. Introduction

In the research of possible new fuels for developing fuel cell technology, the oxidation of small organic molecules on pure platinum and alloys has been widely examined in last years.[1] In particular, ethanol is one of the most-studied molecules due to its advantages.[2-5] It is considered as a 'green' chemical because it can be obtained directly from biomass after distillation, it can be easily introduced in the current fuel distribution system and it has a high energy density in the complete oxidation to CO_2. In this process 12 electrons are exchanged:

$$CH_3CH_2OH + 3H_2O \rightarrow 2CO_2 + 12H^+ + 12e^- \qquad (1)$$

The thermodynamic standard potential of this reaction is 0.085 V, which yields a standard cell potential for an ethanol/oxygen fuel cell of 1.145 V. Nevertheless, there are some problems which should be solved prior to practical use. These problems are related with the slow kinetics of ethanol oxidation reaction that produce large overpotentials, diminishing the operational potential, and with the incomplete oxidation to acetic acid.

Using platinum as a catalyst, studies clearly show that the surface structure is an important parameter that changes significantly the reactivity for the oxidation of small molecules [6-8]. This is the case of ethanol [5, 9]. In acid solutions, the proposed oxidation mechanism has a dual route:



(2)

Reaction steps (1) and (2) represent the route for the incomplete oxidation of ethanol, producing acetaldehyde with two electrons transferred, and acetic acid, transferring two additional electrons. This route should be avoided because acetic acid cannot be oxidized at room temperature. Thus, only 4 electrons are exchanged and 2/3 of the formal energy density of ethanol are not used. To yield CO_2 as final product, it is necessary to break the C-C bond through steps (3) and (4). The cleavage is followed by the transformation of the fragments into adsorbed CO in step (5). CO is considered in many reactions as a poison intermediate because it is adsorbed strongly on the surface and is difficult to oxidize. For that reason, it inhibits further reaction. However, for ethanol oxidation, it can be considered as a previous step in the complete oxidation to CO_2. In acid media and on Pt(111) electrodes, the reaction proceeds exclusively through the route that yields acetic acid whereas Pt (100) electrodes and the stepped surfaces with (110) steps and (111) terraces favor the cleavage of C-C bond and the formation of CO.[5, 9, 10] In addition, foreign adatoms are used to promote the complete oxidation to CO_2, for example, ruthenium, rhodium or tin [11-13].

Nowadays, the research of alkaline fuel cells (AFCs) have regained momentum. The alkaline environment has some advantages. Higher electrocatalytic currents are obtained when compared with acid media and it has lower corrosive properties, which opens up the possibility of using less expensive electrocatalysts.[14] However, the technology of AFCs has to overcome two main problems: the carbonation of the system due to CO_2 retention and the difficulty of finding membranes that can

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sustain operation in alkaline conditions during long periods of time. Nevertheless, new anion exchange membranes have been developed last years for solving these problems.[15-17]

In order to understand the behavior of the possible electrocatalysts, fundamental studies are required. However, there are few studies of ethanol oxidation in alkaline media on platinum electrodes. In only a small number of papers, single-crystal electrodes [18, 19] and polycrystalline surfaces [20, 21] are used. In these investigations, it is clearly stated that the preferred route for the oxidation is that leading to acetaldehyde-acetate production. Additionally, there are some controversies with the oxidation mechanism presented. Koper *et col.* [19] observe the presence of CO_{ads} in the platinum surface using Raman spectroscopy. Conversely, Christensen *et.al* [21] state that no CO_{ads} occurs during the ethanol oxidation in this environment and they propose that the observed signals for CO_{ads} in FTIR are due to a pH changes in the thin layer, which shifts to neutral or acidic values.

In the present paper, we report the influence of the surface structure of Pt single crystals for ethanol oxidation in alkaline media. We use voltammetric and chronoamperometric techniques for study the reactivity of the system and FTIR experiments for finding intermediate and final species formed during ethanol oxidation. These results will be used for understanding the oxidation mechanism on the Pt surfaces.

2. Results

2.1 Ethanol oxidation on Pt basal planes.

Figure 1 shows cyclic voltammetric profiles of Pt single crystal electrodes with basal orientation in alkaline medium, which are in agreement with previous results.[22-27] For these surfaces, the signals appearing in the voltammograms are related to the hydrogen and OH adsorption/desorption processes, aside double layer contributions. These processes are well separated for the Pt(111) electrode and the signals corresponding to the hydrogen adsorption can be found at potentials below 0.4 V whereas OH adsorption occurs at potentials above 0.6 V. For the other two basal planes, both processes overlap and competitive adsorption between hydrogen and OH takes place. For the Pt(100) electrode, signals at potentials below 0.4 V corresponds mainly to the hydrogen adsorption processes whereas OH adsorption occurs mainly above this potential.[24] For the Pt(110) electrode, the peak at 0.27 V in the positive scan direction corresponds to the desorption of a monolayer of hydrogen and the simultaneous adsorption of OH. Of course, the peak in the negative scan direction at 0.25 V corresponds to the opposite process. When compared with acidic solutions in absence of specific adsorption, i.e., in perchloric acid solutions, OH and hydrogen adsorption processes appear in a similar potential range in the RHE scale. However, the detailed shape of the votammograms is markedly affected by the pH.

When ethanol oxidation in 0.1 M NaOH is studied, the measured oxidation currents for the Pt(111) electrode are much higher than those recorded in acidic media (figure 2). The upper potential limit was adjusted to 0.95 V to avoid significant changes in the surface structure due to oxide formation.[28, 29] When the initial voltammogram recorded without ohmic drop compensation (figure 2, dotted line) was compared with those presented in the literature, some differences were found.[18, 19] Maximum currents and peak potentials were different depending on the data source. Due to the large currents and the lower conductivity of the alkaline solutions in comparison with acidic solutions, the ohmic drop in the electrolyte can affect the results. The total resistance of the present cell configuration is ca. 200 Ω and the maximum current is around 1 mA. Thus, it is clear that IR should be corrected to obtain the right voltammogram.[30] It should be noted that resistance in the meniscus can account for more than 80 % of the total resistance due to the small section of liquid in this part. The resistance in the meniscus clearly depends on the electrode area and the meniscus high. Figure 2 shows clearly shows the effect of ohmic drop correction in the ethanol voltammetric profile on Pt (111) in alkaline medium. A well-defined peak at 0.82 V is observed and peak currents as high as 37 mA cm^{-2} were recorded, significantly higher than those previously reported in the literature.

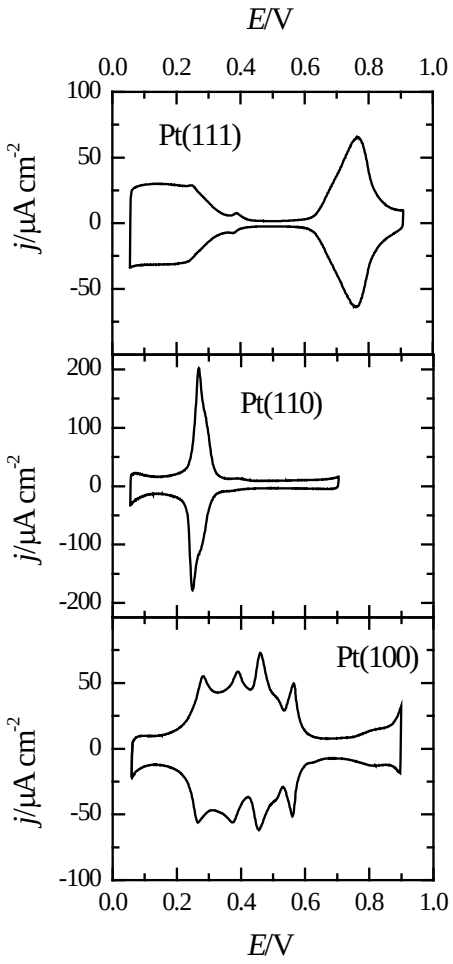

Figure 1. Voltammetric profiles of the Pt(111), Pt(110) and Pt(100) electrodes in 0.1 M NaOH. Scan rate: 0.05 V s^{-1}.

The voltammetric profile for the Pt(111) electrode presents two main characteristics: it has low hysteresis between positive and negative scan directions and the activity diminishes drastically upon cycling (figure 3). In the oxidation of small organic molecules, the hysteresis is normally related to the formation and adsorption of CO at low potentials, which is only

oxidized above 0.7 V.[31] The small hysteresis would then mean that the total amount of CO formed and accumulated on the surface is very small. On the other hand, the deactivation is very significant and after 25 cycles the peak current is only one 20th of that measured in the first cycle. It should be remarked that the deactivation depends on the upper potential limit. When the upper potential limit is set below 0.7 V, the activity remains almost constant upon cycling (not shown).

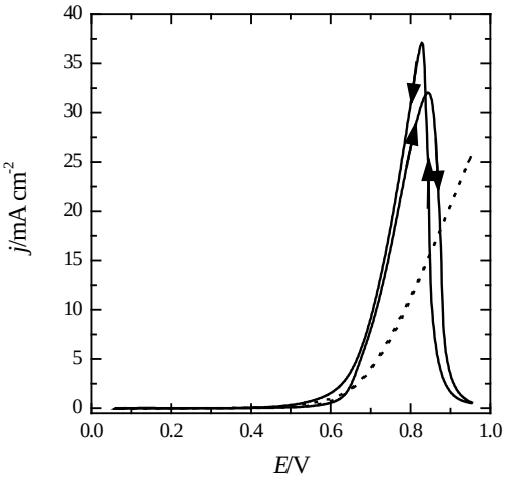

Figure 2. Voltammetric profiles of the Pt(111) electrode (1st cycle) in 0.1 M NaOH + 0.2 M EtOH with (solid line) and without (dotted line) ohmic drop correction at 0.05 V s^{-1}.

For the other two basal planes, the activity is much lower (figure 3). For the Pt(110) electrode, the maximum current is ca. 10 mA cm^{-2}, whereas only 2 mA cm^{-2} is measured for the Pt(100) electrode. In both cases, there is a clear hysteresis in currents and peak potentials. However, this hysteresis is not the typical associated to the formation and adsorption of CO at low potentials. When CO is accumulated on the surface, as happens in the oxidation of ethanol or methanol in acid media,[5, 32] the currents in the positive scan direction are significantly smaller than those measured in the negative scan direction. In the present case, peak currents in the positive scan direction are at least as high as those in the negative scan direction. However, there is a significant shift in region were currents are recorded. This is clearly the case of the Pt(100) electrode; in the positive scan direction, the activity for the oxidation of ethanol is obtained between 0.6 and 0.9 V and the peak current is located at 0.75 V, whereas the significant currents for the negative scan direction are measured between 0.8 and 0.45 V with a peak potential at 0.53 V. Additionally, the deactivation upon cycling is negligible for the Pt(100) electrode. On the other hand, a significant deactivation is observed for the Pt(110) electrode, although to a lesser extent than that aforementioned for the Pt(111) electrode.

It should be highlighted that the activity order for the low index planes is just the opposite of that observed for in acidic media. In acidic media, the order for peak currents is Pt(100)>Pt(110)>Pt(111) whereas in alkaline solutions the order is Pt(111)>Pt(110)>Pt(100). Another important difference is onset potential. In acid solution, the lower onset for the oxidation is observed for the Pt(111) electrode, whereas in alkaline media the lower onset is for the Pt(110) electrode.

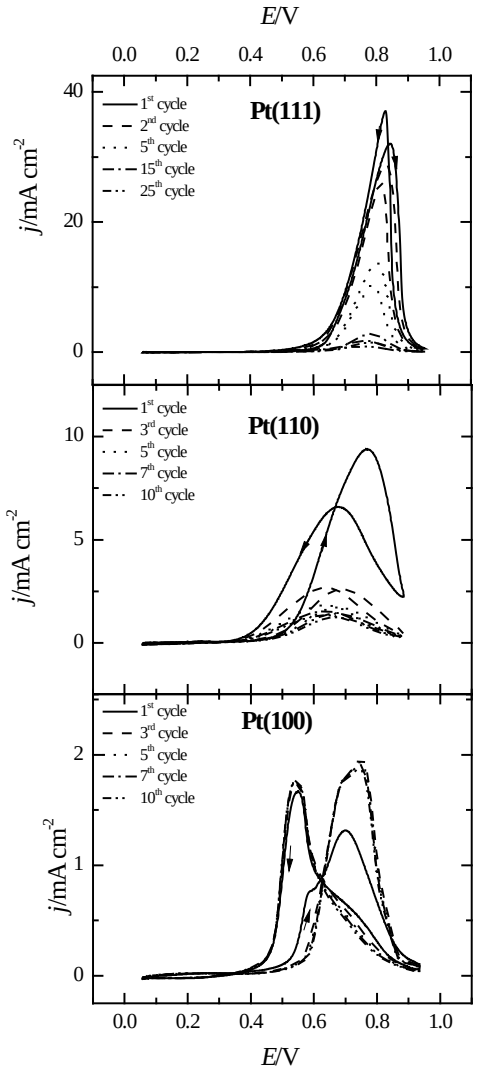

Figure 3. Evolution of the voltammetric profile of the Pt(111), Pt(110) and Pt(100) electrodes upon cycling in 0.1 M NaOH + 0.2 EtOH at 0.05 V s^{-1}.

In order to obtain more information the ethanol oxidation reaction on those electrodes, chronoamperometric experiments were carried out. Figure 4 shows the transients measured at 0.6 V for the basal planes for 10 minutes. This potential was chosen because it is a potential where ethanol oxidation has started but currents are low and are not controlled by the transport limitations of ethanol. Then, the decay in the transients should be related to the presence of adsorbed species blocking the catalytic surface. The currents measured at 0.6 V follow the expected behavior from the currents measured in the voltammetric profiles at 0.6 V. Thus, the largest currents are measured for the Pt(110) electrode and the lowest for the Pt(111) electrode. For all the electrodes, a decay in the currents is observed and it is proportionally larger for the Pt(110) electrode. As aforementioned, this decay is not related to diffusion problems, since the expected limiting diffusion current is more than 10 times larger than the measured here. Additionally, the transient for the Pt (100) electrode shows at short times a small increase in the currents. This process is related to the hysteresis observed in the voltammogram. At 0.6 V currents in the negative scan direction are larger than those in the positive scan direction. Since the transients are recorded after

stepping the electrode from 0.1 V, the initial currents are close to those measured in the positive scan direction at this potential. The current increase is then related to the difference with the negative scan direction. In fact, if the potential is halted at 0.6 V in the positive scan direction during the recording of a voltammogram, currents increase to reach values close to those measured in the negative scan direction.

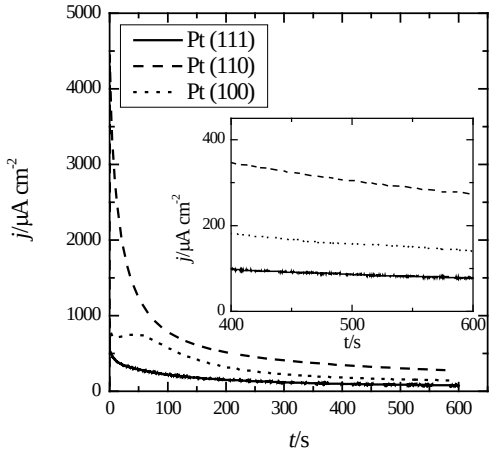

Figure 4. Chronoamperometric transient at 0.6 V for ethanol oxidation on the Pt (111), Pt (110) and Pt (100) electrodes in 0.1 M NaOH + 0.2 M EtOH.

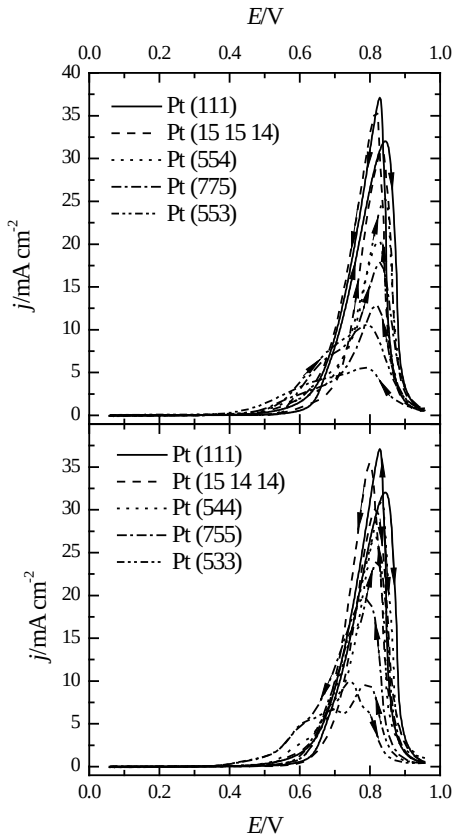

Figure 5. Voltammetric profiles (1st cycle) for Pt stepped electrodes Pt(n,n,n-2) and Pt(n+1,n-1,n-1) in 0.1 M NaOH + 0.2 M EtOH at 0.05 V s^{-1}.

In acidic solutions, it has been found that the presence of steps in the (111) symmetry terrace catalyzes the cleavage of the C-C bond,[9-12] which is the key step in the mechanism for the oxidation of ethanol to CO_2 (or carbonate in alkaline solutions) and higher currents are measured for those electrodes. For that reason, it is interesting to study the effects of the steps in the reactivity of the (111) terraces for ethanol oxidation. Figure 5 shows voltammetric profiles for Pt stepped electrodes. Two series of stepped surfaces containing (111) terraces and (110) or (100) steps were studied. These surfaces are named Pt(s) [(n-1) (111)×(110)]= Pt(n,n,n-2) for the surfaces with (110) steps and Pt(s)[n(111)×(100)]= Pt(n+1, n-1, n-1), for the surfaces with (100) steps. In these notations n represents the number of rows in the (111) terrace. For both series, the presence of steps on the (111) terrace does not improve peak current densities, as can be observed in figure 5. However, the onset potential for the oxidation is displaced towards more negative potentials and the hysteresis between positive and negative scan directions increases. In fact, the behavior of the surfaces with high step density, namely, Pt(553) and Pt(533) electrodes, begin to resemble that of the (110) and (100) surfaces, respectively. In fact, the Pt (533) electrode shows, in the negative scan direction, significant currents until 0.35 V.

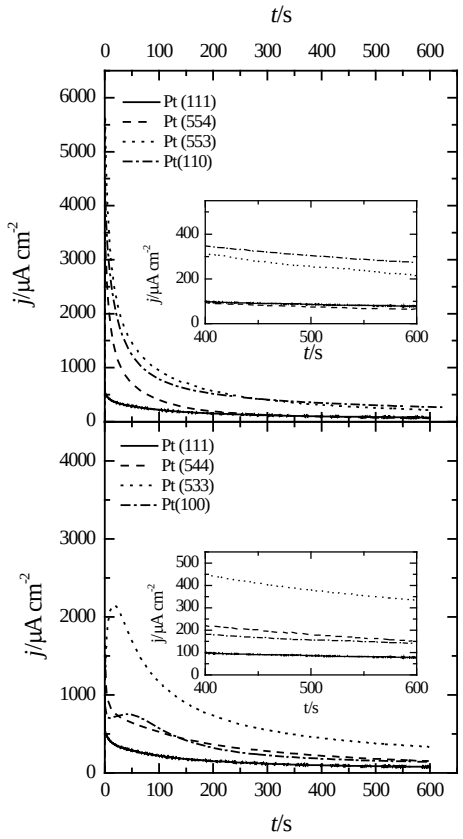

Figure 6. Chronoamperometric transient at 0.6 V for for Pt stepped electrodes Pt(n,n,n-2) and Pt(n+1,n-1,n-1) in 0.1 M NaOH + 0.2 M EtOH.

From these results, it is clear that the activity of these stepped surfaces at high potentials (E>0.6 V) is dominated by the presence of the (111) terraces, whereas the activity at low potentials is dominated by the presence of the steps. In this sense, it can be said that the activity of the (100) step is higher

than that of the (110) step, since currents for comparable step densities in this region are larger in the negative scan direction. In order to demonstrate that, chronoamperometric transients for these series of surfaces were also recorded at 0.6 V (figure 6). As can be seen, the initial current for the series with (110) steps is larger, but the current density decays very fast. On the other hand, for the surfaces with (100) steps, the initial current is smaller, but the decay is also smaller and in some cases, an increase in the currents is observed. This current increase is especially important for surfaces with a (100) high step density, i.e, the Pt(533) surface. As in the case of the Pt(100) surface, the increase has the same origin that the hysteresis observed for the cyclic voltammogram between the positive and negative scan directions. When the activity of the (110) and (100) steps is compared with that of the low index planes, it can be said that the activity of the (100) step is larger than that measured for the Pt(100) electrode at this potential, as figure 6 demonstrates. On the other hand, the activity of the (110) step is similar to that of the Pt(110) low index plane. Thus, the activity order at long times at 0.6 V is the following (100) step>(110) terrace=(110) step>(100) terrace>(111) terrace. The order of reactivity for the steps is also the opposite to that found in acidic media, since (110) steps are more reactive for this reaction than the (100) steps.[9]

2.2 FTIR experiments of ethanol oxidation.

In order to find information about the adsorbates and final products formed during the ethanol oxidation reaction in alkaline medium, FTIR experiments were carried out. Figure 7 shows reference spectra in alkaline solutions for acetate and carbonate, two of the possible final products. It should be mentioned that it is not possible to measure the spectra of acetaldehyde (another possible product) in alkaline solutions since acetaldehyde readily polymerizes through an aldol condensation in this medium. According to the literature,[5, 21, 33] the bands at 1550 and 1415 cm^{-1} for acetate correspond to the O-C-O asymmetric and symmetric stretching vibrational mode, respectively. The band at 1390 cm^{-1} for carbonate is also related to the O-C-O vibrational mode.

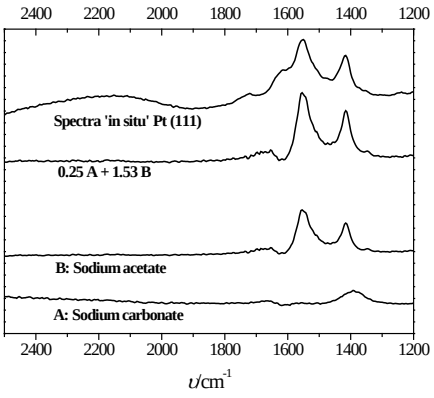

Figure 7. Transmission spectra of 0.2 M acetate and 0.2 M carbonate in 0.1 M NaOH. The spectra of the Pt(111) electrode at 0.8 V in 0.2 M EtOH +0.1 M NaOH is also shown with its adjusted spectra using a linear combination of the carbonate and acetate spectra

For the different electrodes, the spectra at different electrode potentials is shown in figure 8. As can be seen, only acetate bands are visible. It should be highlighted that the band related to adsorbed CO at low potentials cannot be detected. Adsorbed CO on Pt electrodes in alkaline media shows strong bands at ca. 2030 cm^{-1},[34] and this band is not visible in the spectra of all the studied electrodes, even stepped electrodes. As aforementioned, (110) steps are very active for the cleavage of the C-C bond at low potentials producing adsorbed CO in acid solutions.[9, 10] At high potentials, a very small band at 2340 cm^{-1} associated to CO_2 can be observed. The presence of this band is indicative of a large shift in the pH of the thin layer used for the spectra acquisition, due to the oxidation of ethanol trough the reactions of equation (1). At last, the small band present at 1350 cm^{-1} is assigned to acetate group too, according with Zhou experiments.[33]

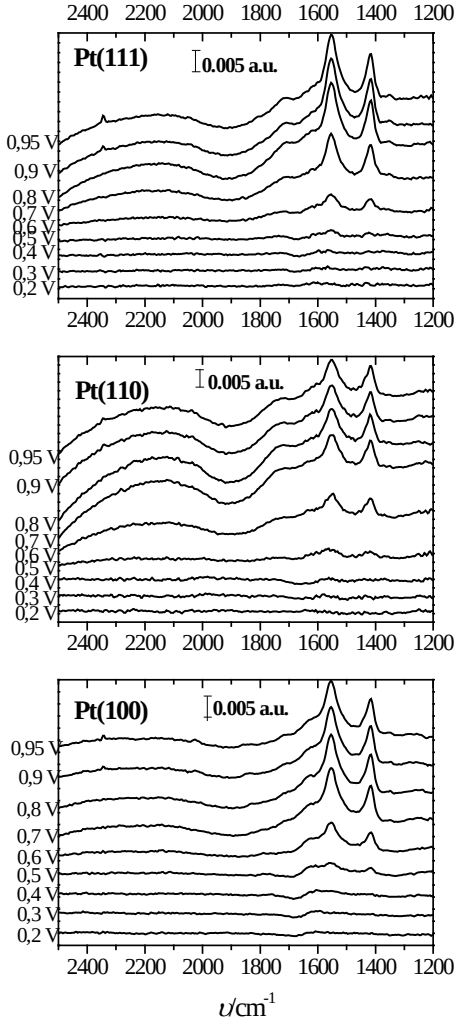

Figure 8. FTIR spectra at different potentials for the Pt(111), Pt (110) and Pt(100) electrodes in 0,2 M EtOH + 0.1 M NaOH. Reference spectra taken at 0.1 V.

In this spectra, the presence of carbonate cannot be discarded a priori, since the carbonate band at 1390 cm^{-1} overlaps with that of 1415 cm^{-1} of acetate, [24, 35] making difficult the correct determination of the ratio CO_2/acetate. For this reason, the reference spectra of carbonate and acetate (figure 7) were

used to fit the measured spectra for the different electrodes.[33] The fitting has been done in the spectral region between 1260 and 1615 cm^{-1} using the spectra for acetate and carbonate as input functions and two adjustable parameters, using the expression:

$$f(\nu) = a \cdot g(\nu) + b \cdot h(\nu)$$

where g(ν) and h(ν) are the spectra of acetate and carbonate, respectively, *a* and *b* two adjustable parameters and f(ν) is the fitting function, which is compared to the experimental spectra for the different electrodes. A least square method is used to determine the two adjustable parameters. The spectra for the Pt(111) at 0.8 V and the calculated fitting are also shown in figure 7. The results for the fittings are presented in Table 1. As can be seen, the amount of carbonate produced in all cases is very low, even for the stepped surfaces which are very active for the formation of CO_2 in acid solutions. Only for the Pt(111) electrode some carbonate can be detected (ca. 14%). This carbonate has been formed above 0.6 V since no CO is detected below this potential value. Thus, it can be concluded that the main products of the oxidation in this medium are acetate and acetaldehyde. These results are in agreement with the absence of CO adsorption bands at low potentials and the results obtained by Christensen *et. al.* [21] with polycrystalline electrodes and suggest that the presence of CO and CO_2 bands are due to depletion of OH^- in the thin layer causing a variation of pH. Thus the preferred route is the incomplete oxidation to acetate.

Table 1. Adjust parameters for the acetate and carbonate spectra for the fitting of the spectra of the different electrodes at 0.8 V.

Electrode	Acetate	Carbonate
Pt (111)	1.53	0.25
Pt (110)	1.22	0.05
Pt (100)	1.39	0.00

3. Discussion

From the results reported in the previous section it is clear that the main product of ethanol oxidation in alkaline solutions is acetate (and possibly acetaldehyde), although the cleavage of the C-C bond to yield CO and CO_2 cannot be completely discarded. Thus, it is important to understand the origin of the important differences when the behavior of these electrodes is compared to that observed in acidic solutions. First of all, the high activity of the Pt(111) electrode in alkaline media is clearly associated with a large production of acetic acid. In perchloric acid solutions, chronoamperometric results also indicate that the activity for acetic acid production is very high at very short times.[5] However, the newly formed acetic acid molecules adsorb immediately on the electrode surface as acetate and inhibit the reaction. In fact, it can be considered a self-poisoned reaction.[5] In alkaline media, the activity is also very high, but acetate adsorption does not occur since the absolute potential is ca. 0.7 V more negative. Thus, the reaction can proceed at a high rate without any obstacle.

Although the reaction on the Pt(111) electrode follows the same mechanism in both media, yielding mainly acetic acid (or acetate, depending on the pH) at a very high rate, there is an important difference in the onset potential in the RHE scale. In acid media, the recorded onset for ethanol oxidation is as low as 0.4 V,[5] but in alkaline solutions is above 0.6 V, the region where OH adsorption on the (111) terrace occurs. In the oxidation of ethanol to acetic acid, an oxygen group should be transferred to the ethanol molecule to give rise to the carboxylic group. This fact suggests that oxidation process in alkaline solutions is triggered by the adsorption of OH on the surface, which is transferred to the ethanol molecule. However, in acidic solutions, adsorbed OH is not required, since the onset for oxidation is at potentials below OH adsorption. In these later media, adsorbed water should then transfer the oxygen group to the ethanol molecule. These differences points out to significant differences in the interfacial water properties (and/or adsorbed OH) between acidic and alkaline interfaces, probably related to the different absolute potential. Similar conclusions have been obtained when reactivity of the single crystal electrodes for the oxygen reduction reaction is studied in acid and alkaline solutions.[36] For this reaction, the reactivity order in acidic and alkaline media are also completely different. Thus, it can be concluded that the different water structure at different pH's and/or the absolute electrode potential affect significantly the reactivity of the species in the interfacial region.

Being acetate the major product, the effect of adsorbed OH can also explain the lower onset for ethanol oxidation for the other basal planes and stepped surfaces in 0.1 M NaOH. The onset for OH adsorption on the Pt(100) and Pt(110) is well below 0.6 V, and therefore, the effective transfer of OH to the ethanol molecule can occur at lower potentials. For the Pt(100), the onset in the negative scan direction is ca. 0.4 V, which coincides with the initial potential for OH adsorption on this plane. For the (110) surface, the onset is even lower in the negative scan direction and in this plane, OH adsorption occurs at potentials as low as 0.26 V.

Another important characteristic of the voltammetric profiles of all the electrodes studied here (except the Pt(111) electrode) is the large hysteresis not related to the formation of CO, as aforementioned. Using Raman spectra and polycrystalline electrodes Koper *et. col.* propose that CH_x species are adsorbed on the electrode surface[19] and these species could be the origin of the hysteresis. They are formed at low potential and block partially the surface inhibiting the oxidation and oxidized at high potentials. However, the spectroscopic signals for these adsorbed species are not accessible in infrared, due to the interference of the window material in the spectral region of interest. For that reason it is not possible to validate this hypothesis, although the possible origin of the signals corresponding to CH_x species will be discussed below. On the other hand, if the oxidation is linked to the presence of OH the surface, it is also possible that the hysteresis could be related to some irreversibility in the OH adsorption. In acid, OH adsorption processes are completely reversible at 50 mV/s, giving rise to a symmetrical voltammetric profile. In alkaline solutions, some irreversibility is observed, since the peak potentials for OH adsorption on the Pt(100) and Pt(110) electrodes is not same in both scan directions. Thus, it could be possible that the presence of ethanol increases the irreversibility of this process, giving rise to a large hysteresis.

Another problem in the oxidation of ethanol in alkaline media is the fast deactivation of the surface. This process cannot be linked to the formation of CO because it has not been detected on

the surface and would have been completely oxidized at the upper potential limit. Thus, another species, which could not be detected by IR, is responsible for the deactivation of the surface. It should be borne in mind that the spectrum for acetaldehyde could not be measured in alkaline solutions due to its reactivity, and for that reason, acetaldehyde formation cannot be detected. However, during the oxidation of ethanol to acetic acid in acidic media, acetaldehyde is always formed. Therefore, in alkaline media, it can be proposed that acetaldehyde is also produced, and this molecule can be the cause for the deactivation after polymerization.

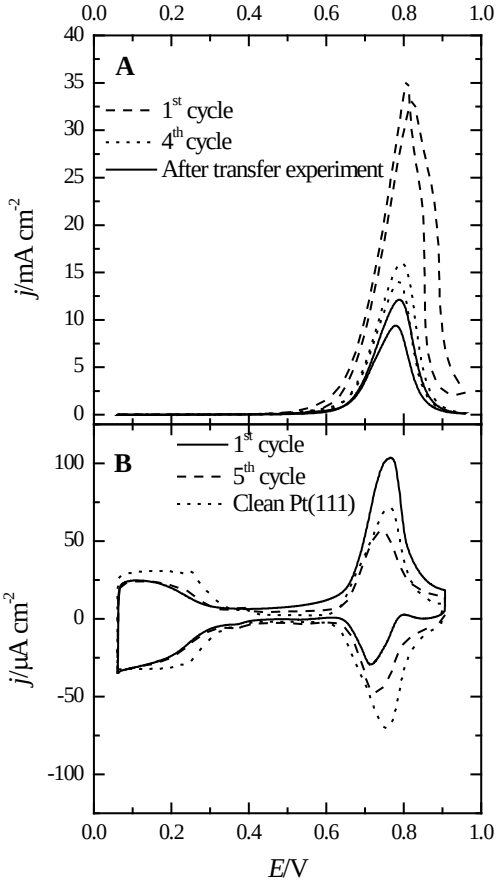

Figure 9. A) Voltammetric profile of a Pt(111) electrode in 0.1 M NaOH+0.2 M EtOH: Dashed and dotted lines: 1st and 4th cycle. Full line, initial cycle after recording experiment in panel B. B) Voltammetric profile of a Pt(111) electrode in 0.1 M NaOH after recording the 4th cycle of panel A. The voltammetric profile of a clean Pt(111) electrode is also shown for comparison (dotted line). Scan rate 0.05 V s^{-1}.

In order to determine the electrochemical properties of this blocking species, and the role of ethanol and acetaldehyde in this process, different voltammetric experiments with ethanol and acetaldehyde were carried out. In the first experiment, four voltammetric cycles for ethanol oxidation are recorded for the Pt(111) electrode (the one with the highest deactivation rate) in 0.1 M NaOH + 0.2 M NaOH (figure 9A dashed lines). After the fourth cycle, a clear deactivation of the surface is observed. Then the electrode is transferred to a cell containing only 0.1 M NaOH and the voltammetric profile is recorded and compared to that obtained for a newly prepared Pt(111) surface (figure 9B). As can be seen, after recording the ethanol oxidation curves, the surface is partially blocked by some species, because hydrogen and OH adsorption charges are smaller than those measured for a clean Pt(111) electrode. In the initial cycle, there is still some ethanol close to the interface and the extra current recorded at E>0.6 V in the first cycle is due to the oxidation of ethanol traces. However, the voltammogram is stable upon cycling and the blocking species cannot be removed if the electrode is cycled up to 0.9 V, even if the lower potential limit is set in the hydrogen evolution region (not shown). Once the profiles in the blank electrolyte are recorded, the electrode is transferred back to the solution containing ethanol (figure 9A, full line). As can be seen, the voltammetric profile corresponds to the one that would have been obtained without the transfer experiment, that is, the profile corresponding to the fifth cycle. Taking into account that the deactivation is linked to the oxidation of ethanol, the species responsible of this deactivation is stable on the surface and does not suffer any oxidation or reduction process at E<0.95 V.

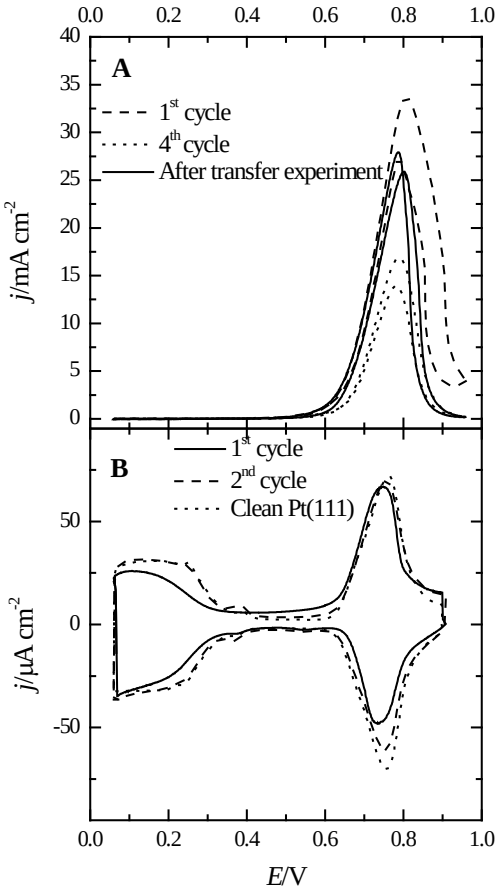

Figure 10. A) Voltammetric profile of a Pt(111) electrode in 0.1 M NaOH+0.2 M EtOH: Dashed and dotted lines: 1st and 4th cycle. Full line, initial cycle after recording experiment in panel B. B) Voltammetric profile of a Pt(111) electrode in 0.1 M NaOH after recording the 4th cycle of panel A and rinsing the electrode with water. The voltammetric profile of a clean Pt(111) electrode is also shown for comparison (dashed line). Scan rate 0.05 V s-1.

If the experiment is repeated but including a rinsing step with water after recording the ethanol oxidation cycles, the curves in figure 10 are obtained. As can be seen, after rinsing the electrode with water, blocking species have been completely removed and the voltammogram of a clean Pt(111) electrode is immediately recovered. Moreover, the initial activity of the electrode for

ethanol oxidation is also recovered, as the voltammetric profile of the electrode after re-immersing the electrode in the ethanol containing solution demonstrates. This experiment indicates that the blocking species does not survive at neutral pHs.

In order to determine the role of acetaldehyde, the same experiments of figures 9 and 10 were recorded, but using a 0.1 N NaOH + 0.2 M acetaldehyde solution. As can be seen in figure 11, acetaldehyde is not oxidized in this medium and the surface becomes instantly blocked by adsorbed species. When the electrode is transferred to the cell containing 0.1 M NaOH, the surface is almost completely deactivated and the adsorbed species are not oxidized or reduced. Only rinsing the electrode with water removes the blocking species, in the same way as observed in figure 10. Thus, it is clear that the diminution of the activity is linked to the production of acetaldehyde. Probably, as soon acetaldehyde is produced, it readily dimerizes and adsorb on the surface, hindering the ethanol oxidation reaction.

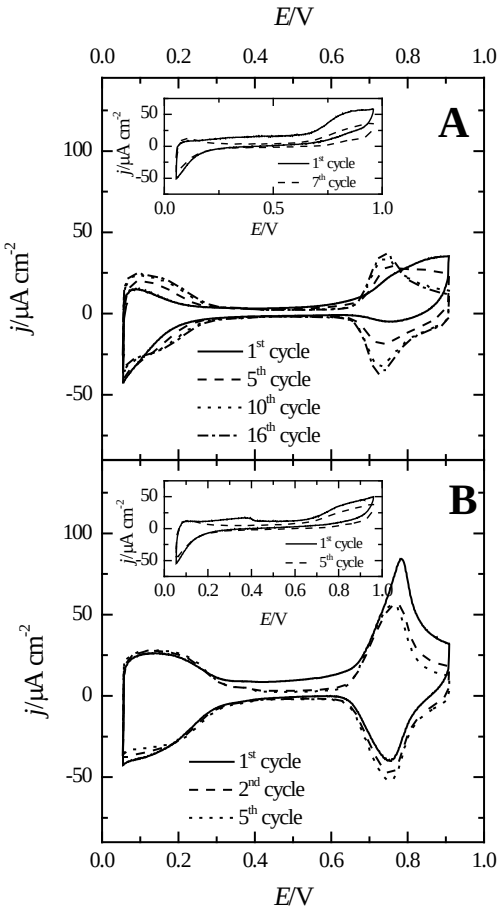

Figure 11. A) Voltammetric profile of a Pt(111) electrode in 0.1 M NaOH after recording the voltammetric profiles in the insert. Insert. Voltammetric profile of a Pt(111) electrode in 0.1 M NaOH+0.2 M acetaldehyde. B) The same as in panel A but rinsing the electrode previously to the immersion in the cell containing 0.1 M NaOH.

This blocking mechanism also explains why the diminution of current upon cycling for follows the order Pt(111)>Pt(110)>Pt(100). This order is also the order of maximum currents. If the inhibition is linked to the formation of acetaldehyde, the higher the currents for the oxidation of ethanol are, the higher the amounts of acetaldehyde are formed. Thus, when the Pt(111) electrode is cycled up to 0.65 V, with low oxidation currents, the poisoning of the electrode is very small, and no poisoning is recorded. Also, it is in agreement with Raman experiments [19], where adsorbed CHx is proposed as the inhibiting species. The CHx is clearly present in acetaldehyde or any polymerization product and can adsorb on the electrode surface. This fact also explains why it has been proposed that the adsorption of CHx adsorbed occurs especially in the (111) domains, because that domains has higher oxidation currents. As has been shown both with voltammetry and chronoamperometry, the higher the currents are, the faster deactivation is observed.

4. Conclusion

The results presented here clearly show that the reactivity of platinum electrodes for ethanol oxidation are affected by the solution pH. The solution pH alters the water structure of the interfacial region and also the absolute potential range in which the oxidation occurs. Both factors clearly changes the reactivity of platinum. In alkaline solutions, higher peak currents are measured, although the selectivity for CO_2 production is much lower. Additionally, the surfaces deactivate fast due to the production of acetaldehyde, which readily polymerizes in this medium and adsorbs on the surface and preventing further reaction.

Experimental Section

Platinum single crystal electrodes were oriented, cut and polished from small single crystal beads (ca. 2 mm in diameter for the voltammetric experiments and *ca.* 4.5 mm for the spectroelectrochemical measurements) following the procedure described by Clavilier and co-workers.[37, 38] The electrodes were cleaned by flame annealing for 30 s in an oxygen/gas flame, cooled down in a H_2/Ar atmosphere and protected with water in equilibrium with this gas mixture to prevent contamination before immersion in the electrochemical cell, as described in detail elsewhere.[38, 39] The voltammetric profiles, and therefore the surface structure of the electrodes, are stable upon cycling provided that oxide formation is avoided.

Voltammetric and chronoamperometric measurements were carried out using a waveform generator (EG&EG PARC 175), together with a potentiostat (Amel Model 2053) equipped with ohmic drop compensation and a digital recorder (eDAQ ED401). For the spectroelectrochemical measurements Nicolet 8700 spectrometer equipped with a MCT (mercury cadmium telluride) detector was used. The spetroelectrchemical cell was equipped with a CaF_2 prism beveled at 60º.[40, 41] IR spectra were collected with a resolution of 8 cm^{-1} and 100 interferograms for increasing the signal-to-noise ratio. A p-polarized light was used in all the FTIR experiments. The spectra are presented as absorbance measurements ($A=-\log (R_1-R_2)/R_1$), where R_2 and R_1 are the reflectance values for the single beam spectra recorded at the sample and the reference potential, respectively. Positive bands in the spectra correspond to species formed at the sample potential, whereas negative bands are referred to species consumed. The sample spectra were collected after applying successive potential steps of 100 mV between 0.10 and 0.95 V. Reference spectrum was always taken at 0.10 V.

Ethanol oxidation experiments were performed in a 0.1 M NaOH + 0.2 M CH_3CH_2OH solution, prepared using ethanol absolute (Merck p.a.), NaOH (NaOH monohydrated 99.99% Merck Suprapur®) and ultrapure water (Elga Purelab Ultra 18.2 MΩ cm). Ar (N50, Air Liquide) was used for desoxygenating the solutions. All the experiments were carried out at room temperature in a three-electrode electrochemical

cell. A platinum wire was used as a counter-electrode and a reversible hydrogen (N50, Air Liquide) electrode was used as a reference electrode (RHE).

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Keywords: Ethanol oxidation · platinum · single crystal electrodes · alkaline solutions · FTIR

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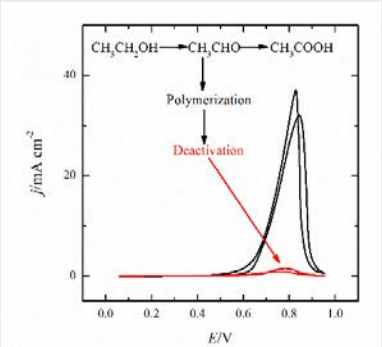
Inverted reactivity order. Ethanol oxidation on platinum single crystal electrodes in alkaline solutions produces mainly acetate and the activity order is the opposite of that found in acid solutions. The formation of acetaldehyde deactivates the surface.



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Ethanol oxidation on Pt single crystal electrodes: Surface structure effects in alkaline medium

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